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Calorimetry and stability field of Mg14Si5O24 anhydrous phase B

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There exist hydrous phase B ($Mg_{12}Si_4O_{19}(OH)_2$) which contains water and anhydrous phase B (Anh-B: $Mg_{14}Si_5O_{24}$) which does not contain water. It is suggested that there is a possibility that Phase B exists in the upper mantle of the earth's interior. Finger et al.(1991) studied the crystal structure of Anh-B. Ganguly and Frost (2006) determined the equilibrium boundary of the reaction, forsterite (Fo: Mg_2SiO_4) + Periclase(Per: MgO) = Anh-B, at 9.0-12.5 GPa and 1173-1873 K, and they used the retrieved Gibbs free energy of formation of Anh-B to calculate the stability field of Anh-B + stishovite (St) with respect to the Mg_2SiO_4 polymorphs. In this study, we synthesized Anh-B by high pressure experiments, measured enthalpies by calorimetry, and calculated the stability field of Anh-B.

Anh-B was synthesized from a 14:5 mixture of MgO and SiO_2 by keeping at 15 GPa and 1723 K for 3 hours, and was recovered after quenching. We identified the sample as Anh-B with powder X-ray and microfocus X-ray diffractometers. We performed calorimetry with Calvet-type calorimeter which was kept at temperature of 978 K, and measured the drop-solution enthalpy of Anh-B with bubbling technique, using lead borate as the solvent.

The measured drop-solution enthalpy of Anh-B was 868(23) kJ.mol^{-1}. The drop solution enthalpy of forsterite was 168.2(9) kJ.mol^{-1}, and that of periclase was 33.7(10) kJ.mol^{-1}(H. Kojitani, unpublished data) Therefore, the enthalpy(delta H_{trans}) for the reaction, 5 forsterite + 4 periclase = Anh-B, was 109(24) kJ.mol^{-1}. We adopted the equilibrium condition of this reaction as 11.1 GPa and 1573 K (Ganguly and Frost, 2006), and calculated delta S_{trans} = -12.6 J.mol^{-1}.K^{-1} from delta H_{trans} and delta V= -11.56 cm^3. Thus the equilibrium boundary of 5 Fo + 4 Per = Anh-B was expressed as P(GPa) = 0.0011(14)T(K) + 9.39. While the slope of this study was less than that of Ganguly and Frost (2006) (P(GPa) = 0.0037T(K) + 6.33), both results are consistent, being the stability of Anh-B in the upper mantle and the transition zone.

Using the delta H_{trans} delta S_{trans}, with publishe data, we calculated the equilibrium boundary of Anh-B = 5 wadsleyite + 4 Per. From delta H_{trans} = 21.58 kJ.mol^{-1}, delta S_{trans} = -3.8 J.mol^{-1}.K^{-1}, and delta V = -4.2 cm^3, it was expressed as P(GPa) = 0.01(2)T(K) + 5.14. Thus, there is a possibility that Anh-B decomposes into wadsleyite and Per at about 17-22 GPa. Ganguly and Frost (2006) discussed the reaction sequence of wadsleyite = Anh-B + St = ringwoodite within the interior of a sufficiently cold slab. However, in this study, we suggest that the reaction would not occur from the above values of enthalpy and entropy of Anh-B.